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Simultaneous voltammetric determination of phenolic antioxidants with chemometric approaches

G.K. Ziyatdinova [a], A.A. Saveliev [b], G.A. Evtugyn [a,*], H.C. Budnikov [a]

[a] Analytical Chemistry Department of Kazan Federal University, Kremlevskaya, 18, 420008 Kazan, Russian Federation
[b] Department of Ecological Systems Modeling of Kazan Federal University, Kremlevskaya, 18, 420008 Kazan, Russian Federation

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ABSTRACT

This work is devoted to the new approach for the description of voltammograms with overlapped peaks of individual analytes. The prediction of individual concentration is achieved by decomposition of entire voltammogram using radial basis function approach followed by fitting the curves using linear model and artificial neural net. The analytical case study is the direct determination of three phenolic antioxidants, i.e., *tert*-butylhydroquinone, 3-*tert*-butyl-4-hydroxyanisole and propyl gallate. The artificial mixtures contained their binary and ternary solutions in the range of concentration from 0.25 to 1.00 mM. The results of decomposition were first checked on similarity of recorded and reconstructed voltammograms followed by determination of individual concentrations by least square method (linear model fitting) and feed-forward artificial net consisting of two hidden layers with 7 and 3 neurons. As was shown, the relative standard deviation of the concentration estimates of 0.03-0.07 can be obtained. The results of prediction were validated using an additional data set with the concentrations of the analytes not used in the fitting procedures.

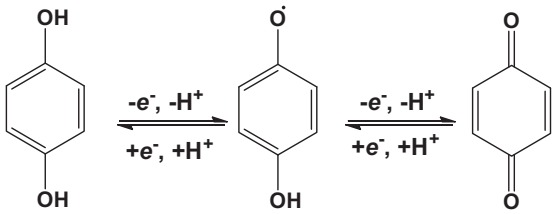
1. Introduction

Phenolic antioxidants are broadly used in the manufacture of resins, polymers, paints, pharmaceutical products and foodstuffs [1,2]. They prevent oxidative destruction of organic matter often followed by formation and accumulation of toxic species by trapping intermediate peroxyl radicals [3]. The reaction results in hydrogen atom transfer (1) and formation of more stable phenoxyl radical which is unable to initiate significant damage of biomolecules (radical scavenging properties).

$$ArOH + ROO^{\bullet} \rightarrow ArO^{\bullet} + ROOH \quad (1)$$

Thus the addition of synthetic phenolics stabilizes the industrial chemicals and improves nutritional value and storage life of the foodstuffs [4]. Meanwhile the exhaustive amounts of antioxidants can provoke radical reactions of oxidative stress due to formation of superoxide anion radical (pro-oxidative effect) [5]. This calls for the development of simple and reliable method of the detection of phenolic compounds in complex matrices to distinguish their antioxidant and toxic influence on a human and hence assess possible risks for health and food safety.

Among other methods, gas liquid and high performance liquid chromatography is most often recommended for the identification and quantification of phenolic compounds [6,7]. The electrochemical oxidation is often complicated with formation of oligomerization products and passivation of the electrodes from noble metals and carbonaceous materials [8,9]. The antioxidants are mainly oxidized by ECE mechanism with formation of quinoid structures as shown in (2) for hydroquinone as an example.



(2)

The oxidation of *p*-substituted and sterically hindered phenols is performed by introduction of hydroxyl group in *ortho*-position followed by formation of *o*-quinone derivative. In some cases, the group in *para*-position is substituted with hydroxyl at intermediate stage and then the reaction proceeds like the hydroquinone or

* Corresponding author.
E-mail addresses: Gennady.Evtugyn@kpfu.ru, gevtugyn@gmail.com (G.A. Evtugyn).

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